

A Periodic Table of Passive Treatment for Mining Influenced Water – Revisited

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Abstract The technical community of regulators and engineers that specializes in passive water treatment design understands that each source of mining influenced water (MIW) has its unique signature, either imposed by the natural geochemical conditions of the ore body and surrounding mine waste, or by resource recovery processes. A passive treatment "decision tree" approach to generic design has been generally accepted in various forms. However, the complexity of MIW lead to the introduction of a "Periodic Table of Passive Treatment" (Gusek 2009) as a useful design tool to satisfy the need to embrace a larger range of MIW chemistries. This paper revisits the concept to include the effects of adsorption and other passive treatment mechanisms.

Keywords MIW, Adsorption, (semi)-Metals

Introduction

The Periodic Table of Elements (PTE) was first introduced by the Russian chemist Dmitri Ivanovich Mendeleev in 1869. Fifty-seven of the elements had been discovered prior to that date, and the rest discovered since then. The scientific and industrial revolution of the 18th and early 19th centuries yielded most of the rest of the elements that Mendeleev categorized. Mendeleev's contribution to science was monumental; he organized the elements into similar groups which we now know are governed by how their atomic structures are arranged. For a more in-depth approach to the PTE from different perspective, the reader is referred to "An Earth Scientist's Periodic Table of the Elements" (Railsback 2004).

The term "mining influenced water" covers the breadth of solutions ranging from what might be termed traditional acid rock drainage (ARD), neutral mine drainage and mining process solutions. The multiplicity of MIW sources compounds the problems facing engineers charged with designing MIW treatment systems. Consequently, every treatment system, whether active or passive, seems to require some site-specific customization. Before passive treatment approaches to various

groups in the PTE can be discussed, it is appropriate to consider the accepted definition of the term "passive treatment". In the past, "constructed wetlands" was in common usage but this term carries much regulatory baggage and does not properly characterize many passive treatment unit processes.

To paraphrase Gusek (2002):

"Passive treatment is a process of sequentially removing contaminants and/or acidity in a natural-looking, man-made bio-system that capitalizes on ecological, and/or geochemical reactions coupled with physical sequestration. The process does not require power or chemicals after construction, and lasts for decades with minimal human help."

Passive treatment systems are typically configured as a series of sequential process units because no single treatment cell type works in every situation or with every MIW geochemistry. It is an ecological/geochemical process because most of the reactions (with the exception of limestone dissolution) that occur in passive treatment systems are biolog-

ically assisted. Lastly, it is a removal process because the system typically provides filtration or immobilization of the metal precipitates that are formed. Without this mechanism, precipitates would be flushed out of the system, and the degree of water quality improvement could be compromised.

Certainly, treating some MIW parameters is considered "easy", such as iron and hydrogen ion (the basic unit of acidity). These parameters have been the focus of typical coal geology derived MIW treatment since the early 1980's. In comparison, "difficult" parameters such as common anions (e.g. sodium, chloride, and magnesium and other components of total dissolved solids [(TDS)] are conserved in traditional passive treatment systems; passive treatment is not considered an appropriate technology. Next are the elements associated with traditional metal mining: iron (again), copper, lead, zinc, cadmium, mercury, and arsenic. These elements are typically found in metal mine ores and wastes as sulfides and passive treatment designers typically focus on

creating conditions favorable to sulfide precipitation such as those found in biochemical reactors (BCRs). That paradigm, however, now has several process alternatives that were not considered in depth in previous work (Gusek 2009).

For the sake of simplicity, the focus of the discussion will be elements and compounds that are problematic or "interesting" ones associated with MIW as summarized in Table 1.

Predominant Treatment Mechanisms in Passive Systems

The following treatment mechanisms are thought to prevail in passive systems addressing "traditional" acidic and alkaline MIW. Carbonate alteration (italicized below) is a passive mechanism that has not been specifically addressed by PTS designers.

- Biological sulfate reduction w/alkalinity improvement
- Metal sulfide formation
- Oxidation

| PTE Group | Elements | Common Aqueous Species/Associated Parameters |
|-----------|--|--|
| 1 | Hydrogen (H), Sodium (Na), and Potassium (K) | TDS, Acidity |
| 2 | Magnesium (Mg), Calcium (Ca), Barium (Ba), Radium (Ra) | TDS, Ra-226 |
| 3 | No traditional MIW elements or compounds | N/A |
| 4 | No traditional MIW elements or compounds | N/A |
| 5* | Vanadium (V) and Uranium (U) [*Actinide Series] | V_2O_6 , U_3O_8 |
| 6 | Chromium (Cr), Molybdenum (Mo) | Cr^{+6} , Cr^{+3} , Mo^{+5} , Mo^{+6} |
| 7 | Manganese (Mn) | Mn^{+2} , Mn^{+4} , Acidity |
| 8 | Iron (Fe) | Fe^{+2} , Fe^{+3} , Acidity |
| 9 | Cobalt (Co) | Co^{+2} , Acidity |
| 10 | Nickel (Ni) | Ni^{+2} , Acidity |
| 11 | Copper (Cu), Silver (Ag), Gold (Au) | Cu^{+2} , Ag^{+2} , AgCN complex, Au -Chloride? AuCN complex, Acidity |
| 12 | Zinc (Zn), Cadmium (Cd), Mercury (Hg) | Zn^{+2} , Cd^{+2} , Hg^{+2} , Hg^{+1} (organic), Acidity |
| 13 | Aluminum (Al), Thallium (Tl) | Al^{+3} , SO_4^{-2} , Tl^{+1} , Tl^{+3} , Acidity |
| 14 | Carbon (C), Lead (Pb) | HCO_3^- , TOC, BOD ₅ , Pb^{+2} , Pb carbonate complex |
| 15 | Nitrogen (N), Phosphorous (P), Arsenic (As), Antimony (Sb) | NH_3 , N_2 , NO_2 , NO_3 , PO_4 , As^{+3} , As^{+5} , multiple As -complexes/ionic species |
| 16 | Oxygen (O), Sulfur (S), Selenium (Se) | O_2 , SO_4 , HS^- , Selenite, Selenate |
| 17 | Fluorine (F), Chlorine (Cl) | TDS |
| 18 | Noble Gases, No traditional MIW elements | N/A |

Table 1 PTE Groups, Elements and Species of Interest in Passive Treatment Systems

- Carbonate dissolution
- Carbonate alteration
- Organic adsorption & complexation
- Plant uptake
- Abiotic adsorption

Conventional wisdom and much research has shown that micro-biologically facilitated reduction and oxidation reactions and carbonate dissolution were the most important removal mechanisms and organic complexation, plant uptake and adsorption play minor as well as temporary roles. This paper not only challenges this misconception but introduces another mechanism: carbonate alteration; e.g. conversion of CaCO_3 to metal carbonates like ZnCO_3 or FeCO_3 .

Passive Treatment System Design Components

From a passive treatment system designer's perspective, there are eight basic components available "off-the-shelf":

- Sulfate reducing bioreactors [AKA compost wetlands, SRBRs, vertical flow ponds, and biochemical reactors (BCRs)]
- Aerobic wetlands,
- Anoxic limestone drains,
- Limestone up-flow ponds,
- Limestone diversion wells,
- Aeration & Settling ponds,
- Successive alkalinity producing systems (SAPS), and
- Open limestone channels & limestone beds.

There may be two more to add to the list: sulfide sequestration cells and iron terraces which might be considered a sub-set of aerobic wetlands.

Each component has its own expected geochemical or biogeochemical capability with respect to mitigating MIW. However, some of these components could exhibit capabilities that have heretofore not been considered within the context of the Periodic Table

of Passive Treatment as first introduced in Gusek (2009).

In Gusek (2009), the oxidation/reduction potential (ORP) was the principal condition that would control whether or not a given MIW parameter would be addressed. This admittedly preliminary approach did not include adsorption phenomena or the displacement/replacement of the calcium ion in calcium carbonate by a metal. The same substitution process may be occurring with the carbonate ion when displaced by fluorine to form fluorite (CaF_2).

Adsorption Processes

Early research (Wildeman et al. 1993) suggested that adsorption processes contributed a small percentage of the overall divalent metal removal performance of passive treatment systems. More recent work by Tebo et al. (2004) and others suggest otherwise. For example, provided that interferences are addressed in pretreatment steps or are not present at all, many divalent metals and other MIW parameters will adsorb to manganese oxide (MnO_2) at neutral pH. Arsenic adsorption to iron oxyhydroxide ($\text{Fe}(\text{OH})_3$) has been observed by many practitioners, including unpublished work by this author. Both phenomena have been found to be microbially facilitated: by Tebo, et al. 2005 in the case of manganese and LaBlanc et al. (1996) in the case of iron oxyhydroxide. See Figs. 1a and 1b for graphical summaries of this process for iron and manganese, respectively. Space limitations preclude inclusion of references for each element. While a separate phenomenon, plant uptake and organic complexation of metals and some MIW parameters are included in this general process for simplicity of discussion.

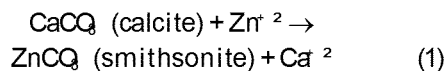
Calcium Carbonate Alteration

The author suspected non-sulfate-reduction mechanisms were responsible for metal removal in one of two pilot scale BCR cells at the Brewer Mine which were described in Gusek

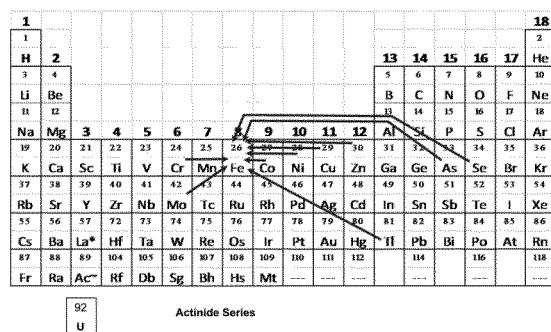
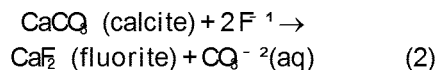
(2000). Sulfate, calcium, and divalent metal mass balance calculations (unpublished) suggested that calcium present in the limestone portion of the BCR substrate was being displaced by some of the divalent metals present, including copper, iron, and zinc. This topic was addressed by Railsback (2010) who provides a thermodynamic stability/solubility plot of some carbonate minerals of divalent cations and an insightful discussion of the effects of atomic radii on this phenomenon. This topic is worthy of modeling investigations by geochemists followed by laboratory and field demonstrations.

An additional calcite/limestone alteration/replacement mechanism is discussed by Turner et al. (2005) for the sequestering of fluorine. Those authors note that some geochemical models (PHREEQ) are ill-equipped to han-

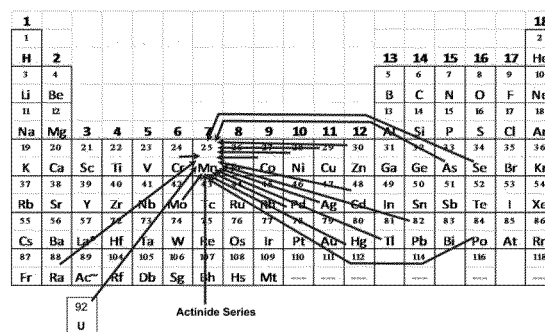
dle this situation because both adsorption and precipitation mechanisms are involved. This process could be used in conjunction with anoxic limestone drains, limestone up-flow ponds, open limestone channels or limestone diversion wells. Equation 1 shows the alteration of calcite to the zinc carbonate mineral smithsonite in the presence of a neutral MIW containing dissolved zinc ions.



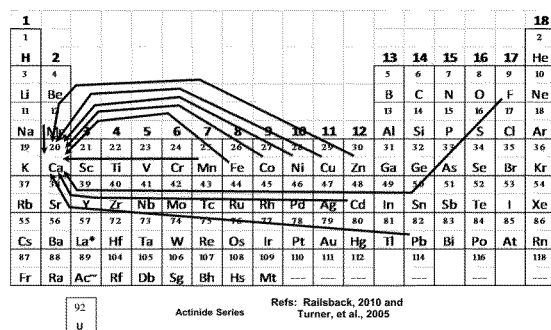
A similar replacement reaction (equation 2) may be responsible for the alternation of calcite to the mineral fluorite.



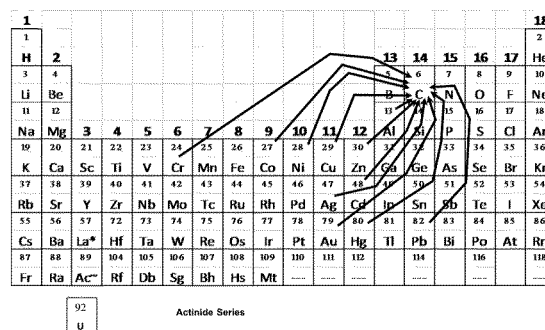
1a Iron Adsorption Tendencies



1b Manganese Oxide Adsorption Tendencies



1c Calcium Replacement/Calcite Alteration



1d Carbon Adsorption/Complexation

Figs. 1a to 1d – Periodic Table of Passive Treatment Adsorption and Replacement/Alteration Tendencies

Column tests by Turner et al. (2008) suggest that pH control is essential for optimizing fluoride removal and that the effects of some interfering ions (e.g. sodium) appear to diminish with time. Also, increased partial pressure of CO_2 (1 atm) in the MIW (e.g. spent pot liner leachate from an aluminum smelting process) also improved the process efficiency. The results were supported by geochemical modeling (PHREEQ) and the process was considered appropriate for designing a permeable reactive barrier.

Periodic Table of Elements Review and Typical MIW Related Elements

Oriented horizontally, the PTE (Figs. 1a to 1d) is organized into seven periods or rows of elements and the Lanthanide and Actinide Series (omitted in Figs. 1a to 1d). Oriented vertically, there are 18 groups or columns of elements. The noble gases are found on the right side of the table; the hydrogen and the anions such as lithium, sodium, and potassium are found on the left side of the table. The elegance of this organization is that the elements of a single group tend to behave similarly in chemical reactions and that applies to behavior in passive treatment systems as well. Why this happens is typically not a concern to passive treatment system design engineers but the fact that it does may need to be more fully embraced.

Discussion

In Figs. 1a through 1d, tendencies of various elements associated with MIW to adsorb to, co-precipitate with, or complex with iron, manganese, calcium, and carbon are indicated by arrows. Due to space restrictions, it is not possible to address the many pre-conditions, interferences, adsorption sequences, that could be involved with these generalized relationships. Probably the most important precondition in most (but not all) adsorptive situations is circum-neutral pH. This is most certainly true in the case of manganese where the virtual absence of dissolved iron is an essential precondition. The partial pressure of carbon

dioxide, P_{CO_2} , and the presence of competing cations are important preconditions with respect to the kinetics and products of calcite replacement/alteration, respectively.

Due to space restrictions, specific references supporting the suspected or documented adsorptive relationships of selected MIW parameters are not included. The multiplicity of mechanisms for a given element suggests that competitive adsorption/replacement/alteration tendencies could make precise predictions with geochemical models difficult. This situation would be further compounded with potential interfering or enhancing conditions. Elevated P_{CO_2} is one example of an enhancing condition with respect to limestone dissolution or alteration. Oxidation reduction potential (ORP) is another.

Turner et al. (2008) employed elevated P_{CO_2} conditions in their work on fluoride removal. Sibrell et al. (2000) employed a similar strategy in enhancing the dissolution of limestone for generating alkalinity. It may be possible to take advantage of this phenomenon with respect to improving passive treatment system designs. Perhaps deep (>33 m) limestone diversion wells could be used to enhance the kinetics of carbonate replacement/alteration reactions at elevated P_{CO_2} ($P > \approx 3$ atm). Maintaining these deep wells would involve periodically exhuming depleted limestone and replacing it with fresh material. Air lift pumping technology could be used to flush-out depleted media. Industrial foams might also be considered for flushing and tremmie placement of fresh media (Masloff 2013).

Summary

The proposed revised Periodic Table of Passive Treatment (PT2) offers another view of the sometimes complicated picture of conflicting situations in treating MIW passively. This overview of a proposed revised PT2 should still be considered an intermediate point on the path to a more complete understanding of the complicated bio-geochemistry behind the passive treatment design process. It should be

considered a logical expansion of the former USBM passive treatment decision tree and like Mendeleev's original work over 130 years ago, should be the focus of future enhancement, perhaps with the inclusion of interfering or enhancing conditions.

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